



# Mechanisms of catalytic ozonation on alumina and zeolites in water: Formation of hydroxyl radicals

Amir Ikhlaiq<sup>a,b</sup>, David R. Brown<sup>a</sup>, Barbara Kasprzyk-Hordern<sup>c,\*</sup>

<sup>a</sup> University of Huddersfield, Department of Chemical and Biological Sciences, School of Applied Sciences, Queensgate, Huddersfield HD1 3DH, UK

<sup>b</sup> University of Engineering and Technology, Institute of Environmental Engineering and Research, Lahore, Pakistan

<sup>c</sup> University of Bath, Department of Chemistry, Faculty of Science, Bath BA2 7AY, UK

## ARTICLE INFO

### Article history:

Received 2 February 2012

Received in revised form 8 April 2012

Accepted 12 April 2012

Available online 21 April 2012

### Keywords:

Catalytic ozonation

Water treatment

Coumarin

7-hydroxycoumarin

ZSM-5 zeolites

Alumina

Mechanism

AOPs

Advanced oxidation processes

## ABSTRACT

The mechanisms of catalytic ozonation of coumarin on ZSM-5 zeolites and  $\gamma$ -alumina in water have been studied. Coumarin is known to react with hydroxyl radicals to produce 7-hydroxycoumarin and is used to differentiate between radical and non-radical mechanisms. The effect of the radical scavenger (t-butanol) and phosphates has also been used to study the possible involvement of radicals and the role of surface hydroxyl groups of catalysts. Four ZSM-5 zeolites with varying silica to alumina ratios and with both hydrogen and sodium counter ions were used in the study (Z1000H:SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 1000, Z900Na:SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 900, Z25H:SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25 and Z25Na:SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25). The results show that both alumina and the zeolites catalyse the removal of coumarin from aqueous solution by ozonation, but that alumina is generally more active than zeolites and it catalyses a radical pathway involving hydroxyl radicals, showing its highest activity at pH close to the point of zero charge where surface hydroxyl groups are most susceptible to conversion of ozone to hydroxyl radicals. The zeolites operate through a simple adsorption process, leading to a direct reaction between adsorbed coumarin and adsorbed ozone. Activity depends to an extent on the silica to alumina ratio of the zeolite but is insensitive to the nature of the zeolite counter ion.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Ozone is a powerful oxidant that can degrade organic pollutants in water. It reacts quickly with organic compounds containing unsaturated bonds and amino groups. However, a single ozonation is not always sufficient for complete mineralization of pollutants. In order to improve ozonation efficiency several advanced oxidation processes (AOP) have been developed, such as O<sub>3</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> [1–4]. In the last few years heterogeneous catalytic ozonation has been successfully used for the removal of organic compounds [5–7]. However, the mechanisms of these processes are still not clear [8,9]. One of the important questions is whether the radical mechanism or direct ozone attack is responsible for the degradation of organic compounds; further investigation is also required to understand the role of adsorption, surface properties of the catalyst used and the effect of pH of water on the efficiency of catalytic ozonation.

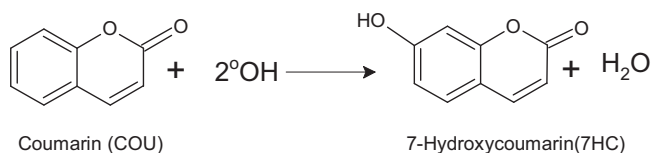
The aim of this study has been to investigate the mechanism of catalytic ozonation (and in particular the formation of hydroxyl radicals) on several ZSM-5 zeolites and alumina. Coumarin (COU)

has been used as a probe molecule as it is known to react with hydroxyl radicals leading to the formation of fluorescent 7-hydroxycoumarin (7HC) (Fig. 1). Coumarin is also a reasonable representative of the constituents in natural organic matter typically found in water [10–12]. Furthermore, it is used in the pharmaceutical industry as a precursor molecule in the synthesis of anticoagulant pharmaceuticals [13]. In this project coumarin was used as a radical probe, to investigate whether the mechanism for the degradation of pollutants on alumina and ZSM-5 zeolites involved the formation of hydroxyl radicals. Previously, various spin traps coupled with transient absorption in UV–vis range and electron paramagnetic resonance (EPR) detection have been successfully applied for the detection of hydroxyl radicals during the ozonation process. Other methods such as luminescence [14], UV–vis absorption [15] and fluorescence [16], have also been applied to measure hydroxyl radicals. Recently, it has been proved that several molecules such as terephthalic acid [17] and coumarin [18–21] produce strong luminescent compounds with hydroxyl radicals. Hence we for the first time used coumarin as a probe molecule for detecting and measuring hydroxyl radicals formed during ozonation in the presence of alumina and ZSM-5 zeolites.

Alumina has been reported by several authors as an effective ozonation catalyst for the degradation of organic acids, chlorinated

\* Corresponding author. Tel.: +44 0 1225 385013; fax: +44 0 1225 386231.

E-mail address: [b.kasprzyk-hordern@bath.ac.uk](mailto:b.kasprzyk-hordern@bath.ac.uk) (B. Kasprzyk-Hordern).



**Fig. 1.** Formation of 7-hydroxycoumarin in the reaction of coumarin with hydroxyl radicals.

organic compounds and chlorinated phenols [22,23], and natural organic matter [5] in water. In contrast, there are some conflicting reports showing a lack of catalytic activity of alumina in, for example, the ozonation of ethers and hydrocarbons [6,24]. Some researchers have found that surface properties of alumina are important in conferring activity in ozonation reactions in water, and surface hydroxyl groups have been identified as being involved in ozone decomposition and free hydroxyl radicals formation [25]. Activity has been shown to be pH dependent with maximum activity corresponding to the pH of zero charge of alumina [26–28]. On the other hand, Lin et al. [29] reported that aqueous ozone is not decomposed by alumina. The work reported in this paper is aimed at clarifying the role of alumina as a catalyst in these reactions, particularly in the terms of the mechanism and whether radical or non-radical mechanisms of ozone degradation are involved.

The catalytic properties of alumina are compared with those of a series of silicalite ZSM-5 zeolites with different silica to alumina ratios and with both sodium and hydrogen counter ions (Z1000H:SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 1000, Z900Na:SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 900, Z25H:SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25 and Z25Na:SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25). Previous work using zeolites as ozonation catalysts has been inconclusive as to whether the zeolites act simply as adsorbents for ozone and for organic compounds, or whether they play a direct part in the decomposition process. Zeolites of this type have been found to be good adsorbents of ozone [30], and have also been shown to be active in the removal of certain organic compounds, including phenol, n-hexadecane and trichloroethene [31–33]. However to date, the mechanisms of removal have not been identified. As stated above, in this research, the activity of these catalysts towards coumarin degradation has been measured, focussing on the production of 7-hydroxycoumarin as an indicator of a radical mechanism. Further experiments have been performed in the presence of tert-butyl alcohol (TBA), which is a known radical scavenger. They have also been performed in the presence of phosphate ions, which may adsorb on the catalyst surface and replace the surface hydroxyl groups of alumina that may be responsible for ozone decomposition [26–28]. Therefore, the effect of phosphates may help to understand the role of surface hydroxyl groups of alumina in catalytic processes and their possible effect on ozonation in the presence of ZSM-5.

## 2. Experimental

### 2.1. Materials and reagents

The ZSM-5 zeolites used in this work were synthesised and supplied by Zeochem (Switzerland).  $\gamma$ -alumina was obtained from Alcoa Inc (USA). Four ZSM-5 zeolites were used in both hydrogen and sodium forms (SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratios denoted 1000, 900 and 25). They are labelled with the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio and the nature of counter ion. Catalysts were used as supplied. Coumarin and 7-hydroxycoumarin were obtained from Sigma–Aldrich. All the chemicals used were of analytical grade and were used without further purification. All the experiments were undertaken with the usage of ultrapure deionised water.

### 2.2. Ozonation experiments

All ozonation experiments were conducted at a temperature of 25 °C in a semi-batch mode (Fig. 2). The concentration of ozone dissolved in aqueous phase was determined with indigo method [34]. Gaseous ozone in in-gas and off-gas was continuously introduced to two sets of glass bottles, each filled with 200 mL of 2% KI, through a ceramic sparger (Fig. 2). After acidification of 200 mL of the 2% KI solution with 10 mL of 1 N HCl, the liberated iodine was titrated with standard 0.005 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> using a starch indicator.

The concentration of ozone dissolved in aqueous phase was determined with indigo method [34]. The difference in absorption of light at 600 nm between blank and sample was measured with a Shimadzu UV-160A UV–vis spectrophotometer. The calibration curve was established before analysis.

Aqueous solution (190 mL) of coumarin (20 ppm) was transferred to the reactor containing 2.0 g of the catalyst and was subsequently stirred (at 200 rpm) over a period of 30 min. Ozone was generated from pure oxygen by an HTL-500GE/20 ozone generator (Azon, Canada) and was continuously introduced to the column by means of a ceramic sparger (flow rate: 0.6 mg/min). Samples were collected at 5 min intervals and were quenched with 0.025 M Na<sub>2</sub>SO<sub>3</sub> in order to remove any residual ozone. All the experiments were performed in the dark and the samples were analyzed immediately after collection.

The ozonation experiments of 7HC were performed as described above. The initial concentration of 7HC was 20 ppm. All samples collected during ozonation (7HC) experiments were diluted with ultrapure water (1 mL of sample was diluted to 25 mL) and were analyzed with a Hitachi F-4500 fluorescence spectrophotometer. The ozonation experiments in the presence of TBA and phosphates were performed as described above by using 50 mg/L of TBA solution or 50 mg/L of sodium dihydrogen phosphate solution.

In order to investigate the effect of catalyst amount on the efficiency of catalytic ozonation, HZSM-5 (Z1000H and Z25H) and alumina were selected. Experiments were performed by undertaking ozonation experiments in the presence of 2.0, 4.0 and 6.0 g of selected catalysts.

### 2.3. Adsorption experiments

The extent to which COU and 7HC were removed from aqueous solution by physical adsorption on the catalysts was measured, so that this effect could be separated from the removal of these compounds by ozonation. For these measurements 2.0 g of the catalyst were added to 190 mL of COU solution (20 mg/L) and stirred for 30 min (rate, 200 rpm). Experiments were performed at 25 °C temperature and samples were collected every 5 min.

### 2.4. Kinetics of aqueous ozone decay

Ozone decay was investigated in pure water (in the absence of COU) in the semi-batch reactor (Fig. 2) and over pH range 3–13. The pH was adjusted using concentrated HCl or concentrated NaOH solution. A saturated solution of ozone was prepared in water (190 mL) by introducing ozone at a rate of 1.5 mg/min for 1 hour in the semi-batch reactor. 0.95 g of catalyst (alumina, ZSM-5 zeolites) was added into 190 mL of ozone-saturated solution (initial ozone concentration: 1.5–3 mg/L, the variable initial ozone concentration is due to the different initial pH of solution), and the mixed suspension was stirred continuously for a period of one hour (temperature: 25 °C). Samples were collected every 10 min, filtered (PTFE 0.45  $\mu$ m syringe filter), quenched with indigo reagent and analyzed for aqueous ozone by indigo method as described in Section 2.2. Aqueous ozone decay was also studied in experiments in which ozonation was used alone without the addition of

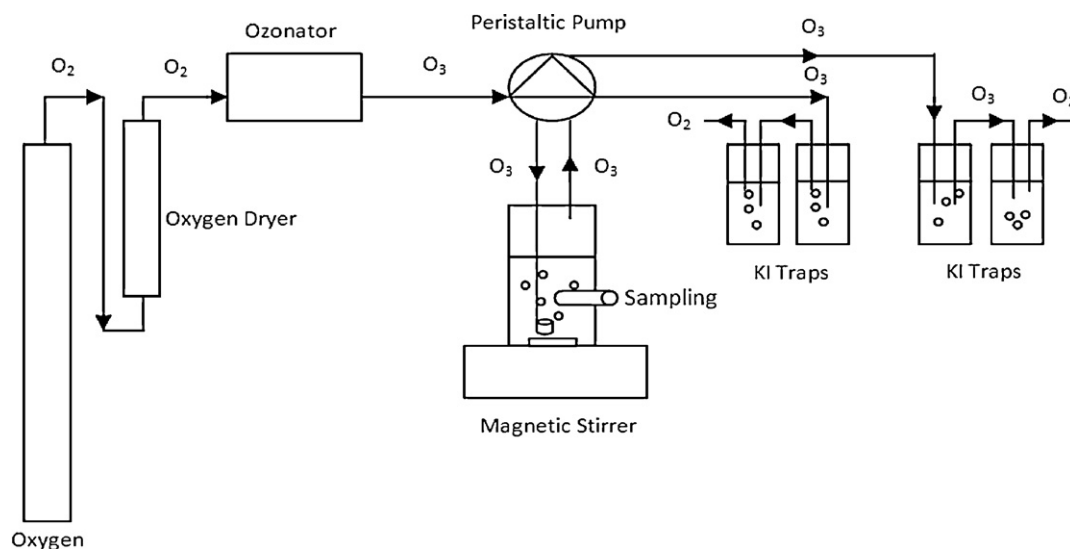


Fig. 2. Scheme of ozonation system.

a catalyst. First order rate constants for ozone decomposition were determined using  $\ln [\text{ozone}]/\text{time}$  plots. Similar experiments were performed in the presence of 50 mg/L of TBA.

## 2.5. Analytical procedures

### 2.5.1. Analysis of coumarin

Coumarin concentration was measured through adsorption at 277 nm (Shimadzu UV-160A UV-vis spectrophotometer) in a 1.0 cm cell following filtration of the working solution, and using a suitable calibration curve. The limits of detection and quantification of the method were 0.06 ppm and 0.09 ppm respectively. The RSD was less than 5%.

### 2.5.2. Analysis of 7-hydroxycoumarin

The concentration of 7HC was determined by fluorescence intensity at 455 nm (excited at 332 nm) using a Hitachi F-4500 fluorescence spectrometer. Both the emission and excitation slits were set to 5.0 nm. A calibration curve was prepared over the appropriate concentration range. Samples were filtered (PTFE 0.45  $\mu\text{m}$  syringe filter) prior to the analysis. The limits of detection and quantification of the method were 0.02 ppm and 0.03 ppm respectively. The RSD was less than 5%.

### 2.5.3. Analysis of phosphates

Phosphate concentrations were determined by ion chromatography using a DIONEX DX-120 system with Ion Pac As14 analytical column (4 mm  $\times$  250 mm) and Ion Pac AG14 guard column (4 mm  $\times$  250 mm) coupled with an ED-50A electrochemical detector (Dionex, USA). Analyses were performed using an isocratic method at a flow rate of 0.82 mL/min and a constant temperature of 30  $^{\circ}\text{C}$ . The injection volume of the sample was 25  $\mu\text{L}$ . The calibration curve was established before analysis. The limit of detection

was 0.5 mg/L. The %RSD for all analyzed phosphate samples was less than 10%.

### 2.5.4. Point of zero charge measurement

The points of zero charge of different catalysts were determined by mass titration method as described by Preocanin and Kallay [35]. Before the measurement, the materials were washed with deionised water and dried in an oven at 108  $^{\circ}\text{C}$ . Subsequently, catalysts (0.1 g) were added to 25 mL of  $10^{-3}$  mol/dm<sup>3</sup> electrolyte solution (NaCl) with continuous stirring. After each portion of the catalyst was added to the solution, the pH of the equilibrated dispersion was measured. The pH of the solution changed gradually and become constant at a certain point and that pH was identified as the point of zero charge ( $\text{pH}_{\text{PZC}}$ ).

## 3. Results and discussion

### 3.1. Characterization of catalysts

The physicochemical properties of the studied catalysts are presented in Table 1. Surface areas and porosities were determined either by the manufacturers or by our group in previous work [6]. They were measured by nitrogen adsorption at 77 K. Surface areas were determined from the desorption isotherms applying the BET equation and porosities were determined from the adsorption isotherms using the Kelvin equation and the BJH method. The surface areas and porosities of the four zeolites are, as expected, essentially the same, and are substantially greater than the surface area of the alumina which, in line with this, exhibits very much larger pores than the zeolites. The  $\text{pH}_{\text{PZC}}$  values for the five catalysts are consistent with compositions, with the zeolites in acid form showing lower values than the sodium forms and the alumina.

Table 1

Physicochemical properties of ZSM-5 zeolites and alumina (data provided by the manufacturer, Zeochem, Switzerland) and obtained from the authors' paper [6]).

Material	SiO <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	Na <sub>2</sub> O (wt%)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mol ratio	Surface area (m <sup>2</sup> /g)	Average pore size (Å)	Crystal size ( $\mu\text{m}$ )	Point of zero charge (pH)
Z900Na	98	0.2	1.3	900 $\pm$ 5	300	5.3	2–5	9.2 $\pm$ 0.1
Z25Na	90	5.4	3.7	30 $\pm$ 5	300	5.3	<1	9.5 $\pm$ 0.1
Z1000H	99	0.1	0.04	1000 $\pm$ 5	300	5.3	<1	7.5 $\pm$ 0.2
Z25H	90	5.4	0.1	30 $\pm$ 5	300	5.3	<1	5.0 $\pm$ 0.2
Alumina	0	100	0	–	190	47.8	–	8.9 $\pm$ 0.1

### 3.2. Adsorption of coumarin on $\text{Al}_2\text{O}_3$ and ZSM-5 zeolites in the absence of ozone

The data appears in Fig. 3 and is shown as the percentage of total coumarin concentration removed from solution with time in the reactor, at various pHs. The data shows clearly that the four zeolites adsorb coumarin to a similar extent and more effectively than alumina. There is relatively little dependence of adsorption capacity on solution pH. After 30 min, the zeolites typically adsorb 25% of the coumarin at pH 3.0 and 15% at pH 13.0, whereas the alumina adsorbs 5% or less at both pHs. It is worth noting that adsorption of 5% of the coumarin corresponds to only 0.5 mg coumarin per gram of catalyst. Additionally, the first order rate constants of coumarin adsorption on alumina and zeolites at different pH values have been determined. Referring to Table 3, the rate constants of coumarin adsorption on ZSM-5 zeolites and alumina are consistent to some extent over the pH range 3.0–8.8, but in all cases, show a dramatic fall at pH 13.0. It is likely that the surface is fully populated with  $\text{OH}^-$  ions at this pH and we suggest that this phenomenon might result in reduction of the rate of adsorption of coumarin.

### 3.3. Catalytic ozonation of coumarin and the effect of pH

The pH of solution plays an important role in understanding of the mechanisms of catalytic ozonation, since it affects ozone decomposition. Furthermore it determines surface properties of catalysts and properties of analytes being oxidised. Ozonation reactions at different pH follow different mechanisms. It is well-known that the presence of  $\text{OH}^-$  ions in water leads to ozone decomposition and generation of hydroxyl radicals ( $\cdot\text{OH}$ ), which then react with organics in a non-selective way [36]. The pH of solution could also affect the surface properties of catalysts such as metal oxides. Alumina is a good example. At basic pH ( $\text{pH} > \text{pH}_{\text{PZC}}$ ) the surface of alumina is negatively charged (no surface hydroxyl groups present), at acidic pH ( $\text{pH} < \text{pH}_{\text{PZC}}$ ) its surface is positively charged, while at  $\text{pH} = \text{pH}_{\text{PZC}}$  the surface of alumina is neutral (surface hydroxyl groups with no charge) [37].

The pH of solutions may also change the surface properties of zeolites. For example, Valdes et al. [38] reported that pH of solution can affect the aqueous ozone decay rates in the presence of zeolites. It was stated that at  $\text{pH} > \text{pH}_{\text{PZC}}$  zeolites are negatively charged and Lewis acid sites may be responsible for ozone decay. On the other hand at  $\text{pH} < \text{pH}_{\text{PZC}}$  the surface will be positively charged and Bronsted acid sites on zeolites may be responsible for aqueous ozone decay and generation of hydroxyl radicals [38]. It has to be however noted here that zeolites (and aluminas) do not exhibit Lewis acidity in the presence of water as Lewis sites hydrate and become Bronsted sites [39,40]. It is therefore important to investigate the effect of pH in order to understand the mechanism of catalytic ozonation processes.

Fig. 4 shows the percentage removal of coumarin with time for the same catalysts and at the same pH values (as in Section 3.2) but in the presence of ozone. Data is also shown for percentage removal under the action of ozone alone. The first thing to note is that at pH 13.0, ozonation is effective at decomposing coumarin, producing 60% removal after 30 min, but the presence of the catalysts does not affect the extent of decomposition. At lower pH the catalysts have an effect. By considering the difference between ozonation alone and ozonation in the presence of a catalyst, alumina is most effective at pH 8.8 (Fig. 4e). The zeolites have a relatively small effect at this pH, with the low silica zeolites having almost no effect and the high silica zeolites similar to the alumina. As the pH is reduced the activity of the zeolites increases and at pH 3.0 all the zeolites lead to complete removal of the coumarin after 30 min compared to ozonation alone and ozonation/alumina which lead to only 30–40% removal.

It is possible to rationalise these results to some extent. At pH 13.0, none of the catalysts show activity. This is most likely because they are all well above their  $\text{pH}_{\text{PZC}}$  and their surfaces are essentially covered with hydroxide ions. It is known that hydroxide ions promote the decomposition of ozone so any reaction of coumarin with ozone on the surface of the catalysts would be unlikely.

Alumina shows its maximum activity at pH 8.8, close to its  $\text{pH}_{\text{PZC}}$  of 8.9. This suggests that the most active surface for catalytic ozonation is that which might be dominated by neutral hydroxyl groups. This pH dependence of alumina's activity has been noted before [26–28].

The zeolites appear to be most active at acidic pHs. For example the removal of COU on studied zeolites was 90% at pH 3.0 and only 68% at pH 13.0 (Fig. 4). It has been suggested by others that Bronsted acid groups on zeolites might promote ozone decay and even lead to the generation of hydroxyl radicals. This possibility is investigated in the following experiments. It is also worth noting that the pH of solution did not change significantly ( $\pm 0.1$ ) after 30 min ozonation with and without catalysts.

### 3.4. Formation of 7-hydroxycoumarin

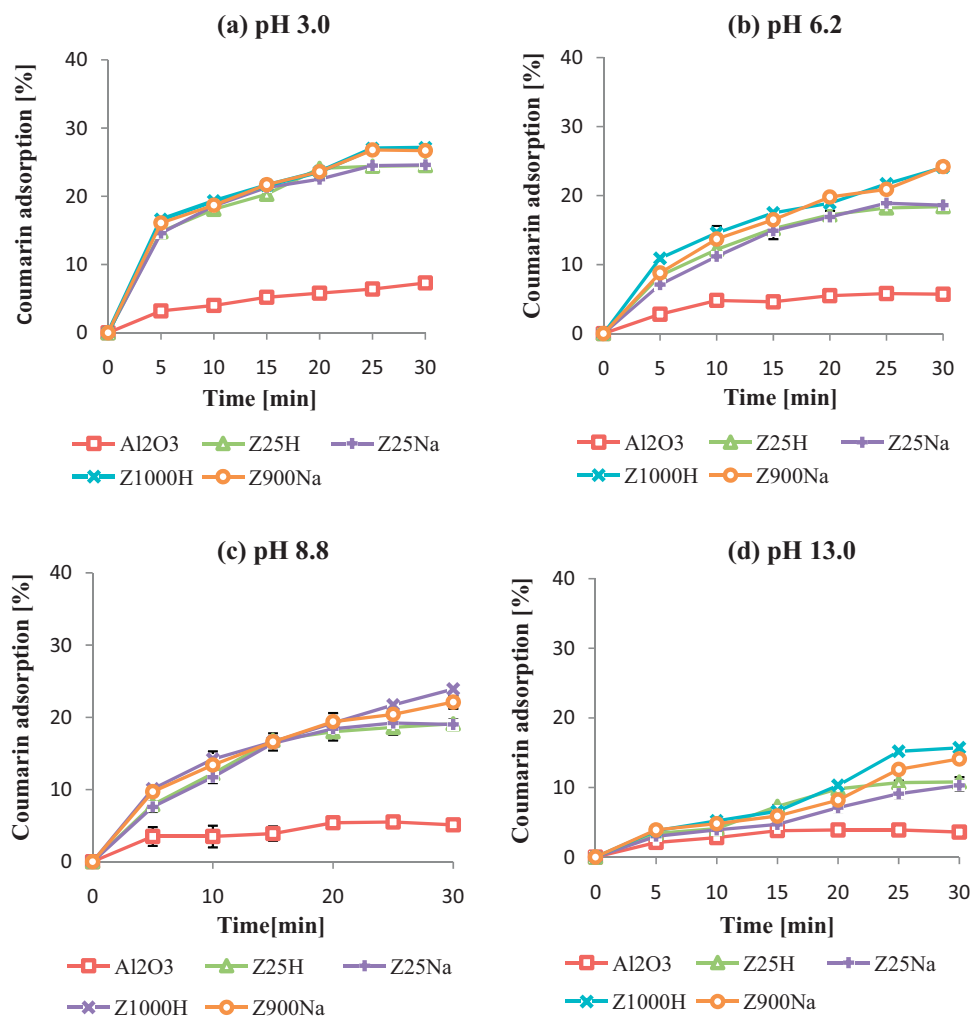
The formation of 7HC, a hydroxylated transformation product of COU, was monitored during ozonation of coumarin. This product is thought to be an indicator of a radical mechanism of decomposition. The data appears in Fig. 5. This shows that, at pH 3.0, almost no 7HC is formed with any of the catalysts, suggesting that decomposition does not involve a radical mechanism at this pH. At pH 6.2 and 8.8, alumina results in significant 7HC generation, in contrast to the zeolites which result in negligible amounts of the product. This strongly suggests that alumina does indeed promote decomposition of coumarin by a radical mechanism, at least at a pH close to the  $\text{pH}_{\text{PZC}}$ . Based on several reports [33–36], it is assumed that superoxide ion,  $\text{HO}_2\cdot$  and  $\text{H}_2\text{O}_2$  do not interfere with the reaction between hydroxyl radicals and COU to produce 7HC. Additionally, in this work a mixture of 5 mL of 30%  $\text{H}_2\text{O}_2$  and 195 mL of 20 mg/L COU was treated in a semi-batch reactor for 30 min and no significant fluorescence was observed.

It is interesting that the profiles shown in Fig. 5b and c for alumina indicate that the 7HC concentration rises over the first 10–15 min and then decreases. It seems likely that this decrease is due to subsequent reaction of 7HC with more ozone, perhaps under catalytic action. Although we suspect that the low yield of 7HC reflects a relatively low concentration of formed hydroxyl radicals, an alternative explanation could be that negligibly low fluorescent isomers of 7HC are formed in its place. Other researchers have detected following isomers 3HC, 4HC, 5HC, 6HC and 8-hydroxycoumarin [19].

At the highest pH of 13.0, the zeolites also appear to promote the formation of 7HC. Because the zeolites are so far above their  $\text{pH}_{\text{PZC}}$  for this process, it seems that however 7HC is produced the mechanism under zeolite catalysis is different to that associated with alumina. In fact, it is likely that the high concentrations of hydroxide ions at pH 13.0 may simply be acting as precursors for hydroxyl radicals, quite independently of whether a catalyst or which catalyst is present.

### 3.5. The aqueous ozone depletion

The concentration of ozone in solution during the reaction of coumarin is shown in Fig. 6. Monitoring of aqueous ozone concentrations in coumarin ozonation experiments undertaken at pH 3.0, 6.2 and 8.8 revealed that the highest concentrations of aqueous ozone were observed during ozonation alone, decreased during ozonation in the presence of zeolites, and were the lowest in the presence of alumina. At pH 13.0 aqueous ozone concentrations



**Fig. 3.** Removal of coumarin by adsorption ( $C_{0(\text{COU})} = 20 \text{ mg/L}$ ;  $T = 25^\circ \text{C}$ ; pH 3.0, 6.2, 8.8 and 13.0; adsorbent = 2.0 g;  $V = 190 \text{ mL}$ ,  $\text{SD} \pm 1.5\%$ ).

were at a similar level in all studied ozonation systems (Fig. 6). Low concentrations of aqueous ozone in the presence of alumina are an indication that its decay rate is higher in the presence of alumina.

Further experiments were performed to investigate the rate at which ozone decomposition (or at least ozone removal) occurs on the alumina and zeolite studies in the absence of any organic compounds, the idea being that at least part of the ozone reduction observed as coumarin is removed might in fact be due simply to decomposition of ozone on the catalyst surface. First order rate constants for the decomposition of ozone in the presence and absence of the five catalysts studied are shown in Table 2 (data is also shown for the rates of ozone decomposition in the presence of TBA, referred to later). Rate data for the decomposition reaction without

TBA shows that at pHs 3.0 and 6.2 the catalysts do catalyse ozone decomposition, and alumina appears to catalyse the process more effectively than the zeolites. At pH 13 the rates for all studied systems are similar. The fast decay of aqueous ozone at pH 3.0 and 6.2 in the alumina/ozone system may be due to the interaction of aqueous ozone with the surface hydroxyl groups of alumina. It is reasonable that this effect is not observed at pH 13, where the pH is much higher than the  $\text{pH}_{\text{PZC}}$  of alumina, and where the surface would be negatively charged.

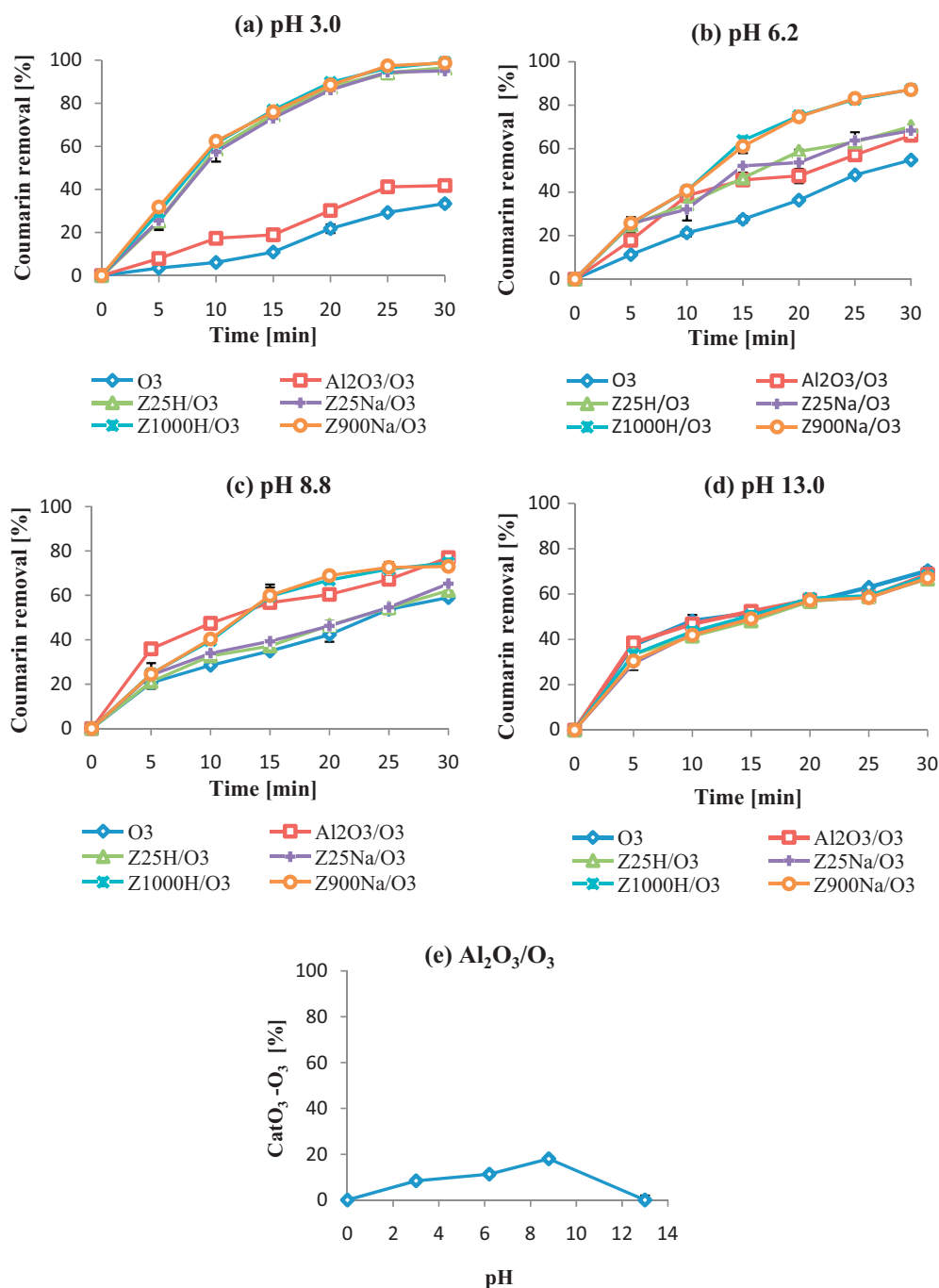
In contrast to our results, it has been reported by Lin et al. [29] that aqueous ozone is not decomposed by alumina. On the other hand other authors have observed aqueous ozone decay in the presence of alumina [5,22,23]. Researchers have claimed that aqueous

**Table 2**

Effect of TBA and pH of solution on the first-order ozone decay rate constants in the presence and absence of alumina and ZSM-5 zeolites.

Process	$k_{\text{overall}} \times (10^{-3} \text{ s}^{-1})$		$k_{\text{overall}} \times (10^{-3} \text{ s}^{-1})$		$k_{\text{overall}} \times (10^{-3} \text{ s}^{-1})$	
	pH 3		pH 6		pH 13	
	No TBA	With TBA	No TBA	With TBA	No TBA	With TBA
$\text{O}_3$	$0.38 \pm 0.03$	$0.35 \pm 0.003$	$0.66 \pm 0.01$	$0.51 \pm 0.01$	$4.1 \pm 0.1$	$3.1 \pm 0.2$
$\text{O}_3/\text{Alumina}$	$0.61 \pm 0.03$	$0.41 \pm 0.01$	$0.98 \pm 0.06$	$0.64 \pm 0.02$	$4.2 \pm 0.1$	$2.9 \pm 0.2$
$\text{O}_3/\text{Z 25H}$	$0.52 \pm 0.02$	$0.47 \pm 0.08$	$0.86 \pm 0.03$	$0.77 \pm 0.05$	$4.3 \pm 0.3$	$3.1 \pm 0.3$
$\text{O}_3/\text{Z1000H}$	$0.46 \pm 0.01$	$0.43 \pm 0.01$	$0.77 \pm 0.04$	$0.70 \pm 0.03$	$4.3 \pm 0.1$	$3.3 \pm 0.3$
$\text{O}_3/\text{Z25Na}$	$0.47 \pm 0.03$	$0.43 \pm 0.01$	$0.76 \pm 0.04$	$0.71 \pm 0.04$	$4.3 \pm 0.2$	$2.9 \pm 0.2$
$\text{O}_3/\text{Z900Na}$	$0.45 \pm 0.01$	$0.43 \pm 0.01$	$0.75 \pm 0.02$	$0.72 \pm 0.06$	$4.3 \pm 0.1$	$3.1 \pm 0.3$



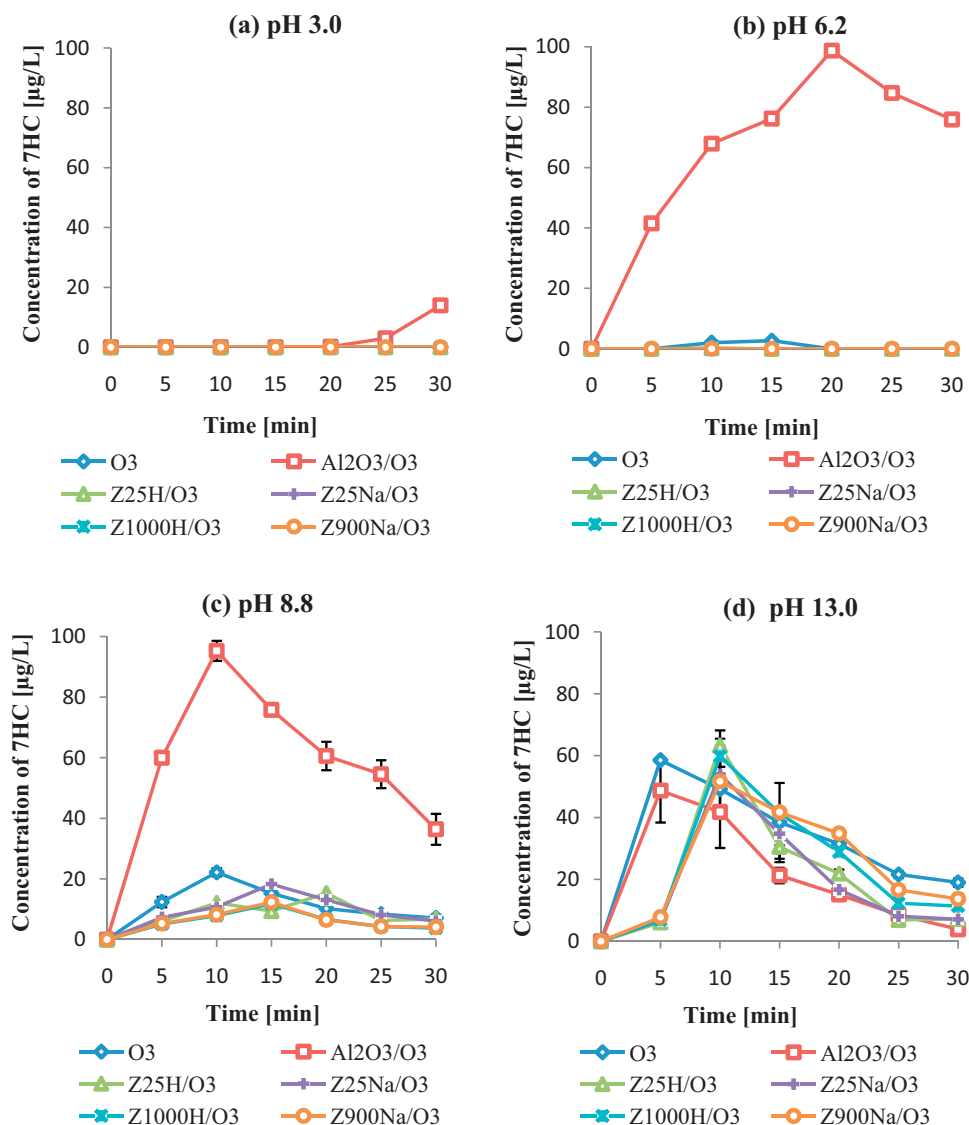


**Fig. 4.** Removal of coumarin by ozonation alone and ozonation in the presence of  $\text{Al}_2\text{O}_3$  and ZSM-5 zeolites ( $C_{0(\text{Cou})} = 20 \text{ mg/L}$ ;  $T = 25^\circ\text{C}$ ; pH 3.0, 6.2, 8.8 and 13.0;  $\text{O}_3 = 0.6 \text{ mg/min}$ ; catalyst = 2.0 g;  $V = 190 \text{ mL}$ ;  $\text{SD} \pm 5\%$ ).

**Table 3**

Effect of pH of solution on the first-order coumarin adsorption rate constants in the presence of alumina and ZSM-5 zeolites.

Coumarin adsorption $k$ overall $\times (10^{-4} \text{ s}^{-1})$					
pH	Z1000H	Z900Na	Z25H	Z25Na	Alumina
3.0	$1.51 \pm 0.02$	$1.51 \pm 0.03$	$1.38 \pm 0.02$	$1.37 \pm 0.03$	$0.37 \pm 0.02$
6.2	$1.34 \pm 0.03$	$1.41 \pm 0.02$	$1.06 \pm 0.02$	$1.14 \pm 0.02$	$0.30 \pm 0.02$
8.8	$1.31 \pm 0.01$	$1.28 \pm 0.04$	$1.13 \pm 0.06$	$1.17 \pm 0.05$	$0.26 \pm 0.01$
13.0	$0.96 \pm 0.03$	$0.80 \pm 0.02$	$0.67 \pm 0.01$	$0.59 \pm 0.02$	$0.19 \pm 0.02$



**Fig. 5.** Formation of 7-hydroxycoumarin as a result of ozonation of coumarin ( $C_{0(\text{cou})} = 20 \text{ mg/L}$ ;  $T = 25^\circ\text{C}$ ; pH 3.0, 6.2, 8.8 and 13.0;  $O_3 = 0.6 \text{ mg/min}$ ; catalyst = 2.0 g;  $V = 190 \text{ mL}$ ; excitation wavelength = 332 nm; emission wavelength = 455 nm; SD  $\pm 5 \text{ µg/L}$ ).

ozone decay on alumina at pH close to the  $\text{pH}_{\text{PZC}}$  involved hydroxyl radicals, which increased the rate of ozone decay [26–28].

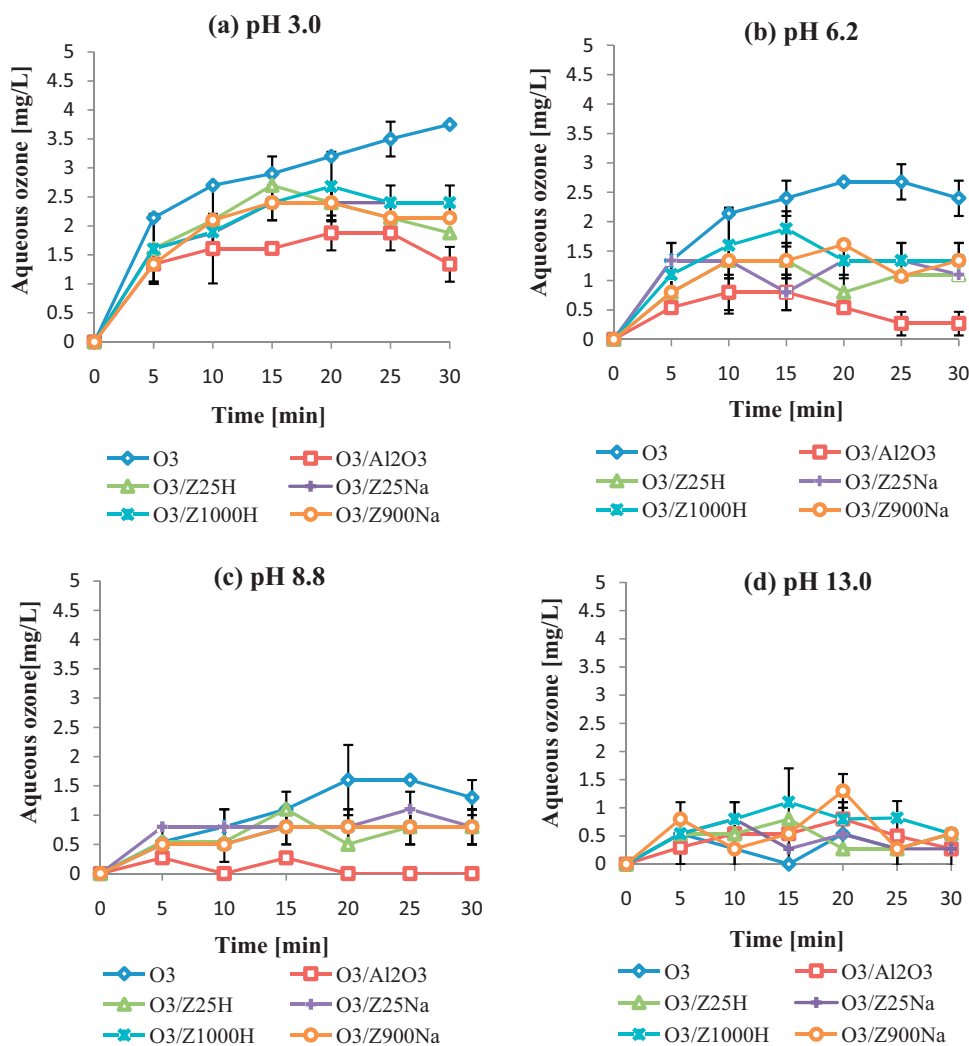
Table 2 shows that the zeolite catalysts have a less pronounced effect on ozone decomposition than alumina. The previous observation that zeolites tend not to promote radical mechanisms (coumarin removal results in relatively little 7HC production) suggests that reductions in ozone concentration may be due to adsorption on the zeolite surface rather than by ozone decomposition on the surface. Indeed, Fujita et al. [30] found that high silica zeolites reduce the aqueous ozone concentrations and proposed that it may be due simply to the adsorption of ozone. Others in contrast [38] reported that acid sites on zeolites might be responsible for aqueous ozone decomposition.

Staying with Table 2, the effect of the radical scavenger TBA on the rate of ozone removal can be seen. The results show clearly that at pH 3.0 and 6.2, TBA reduces the rate of ozone removal on alumina but has no significant effect on ozone loss over the zeolites. This is yet more evidence for a radical ozone decomposition method with alumina but a non-radical route with zeolites.

At the highest pH of 13.0, TBA reduces ozone loss over all catalysts and, importantly, in the absence of any catalysts, to about the same extent. This is almost certainly a consequence of the high hydroxide ion concentration in solution at this pH, which will inevitably lead to the generation of hydroxyl radicals independent of whether a catalyst is used or not.

### 3.6. Effect of hydroxyl radical scavengers

The evidence presented above suggests that ozonation of organic compounds under catalysis by alumina takes place, at least to an extent, by a radical mechanism, and that the same reactions under zeolite catalysis probably take place by a simple adsorption process in which reaction occurs on the catalyst surface between adsorbed ozone and the organic compound. Further experiments to investigate this were carried out by observing the effect of the radical scavenger, TBA, on the rate of removal of coumarin and the rate of production of 7HC. The data was taken at pH 6.2 and is shown in Fig. 7. The TBA is a hydroxyl radical scavenger and reacts with



**Fig. 6.** Aqueous ozone concentration during ozonation alone and ozonation in the presence of  $\text{Al}_2\text{O}_3$  and ZSM-5 zeolites ( $C_{\text{O}(\text{COU})} = 20 \text{ mg/L}$ ;  $T = 25^\circ\text{C}$ ; pH 3.0, 6.2, 8.8 and 13.0;  $\text{O}_3 = 0.6 \text{ mg/min}$ ; catalyst = 2.0 g;  $V = 190 \text{ mL}$ ;  $\text{SD} \pm 0.3 \text{ mg/L}$ ).

•OH radicals with a rate constant of  $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [41]. It reacts directly with ozone with a rate constant of  $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [42].

Comparing Fig. 7a and b shows that TBA reduces the rate of removal of coumarin both under ozonation alone and under ozonation in the presence of alumina. This suggests that alumina-catalysed ozonation involves a radical mechanism. In contrast, in the presence of all four of the zeolites, TBA has a negligible effect on the rate of coumarin removal (Fig. 7c). This data suggests strongly that alumina catalyses a radical mechanism and the zeolites operate by a mechanism in which radical processes are not important. Fig. 7d provides further evidence as it shows that the production of 7HC by alumina-catalysed ozonation is stopped altogether by the presence of TBA, consistent with 7HC being produced over alumina by a radical mechanism which is suppressed by the radical scavenger.

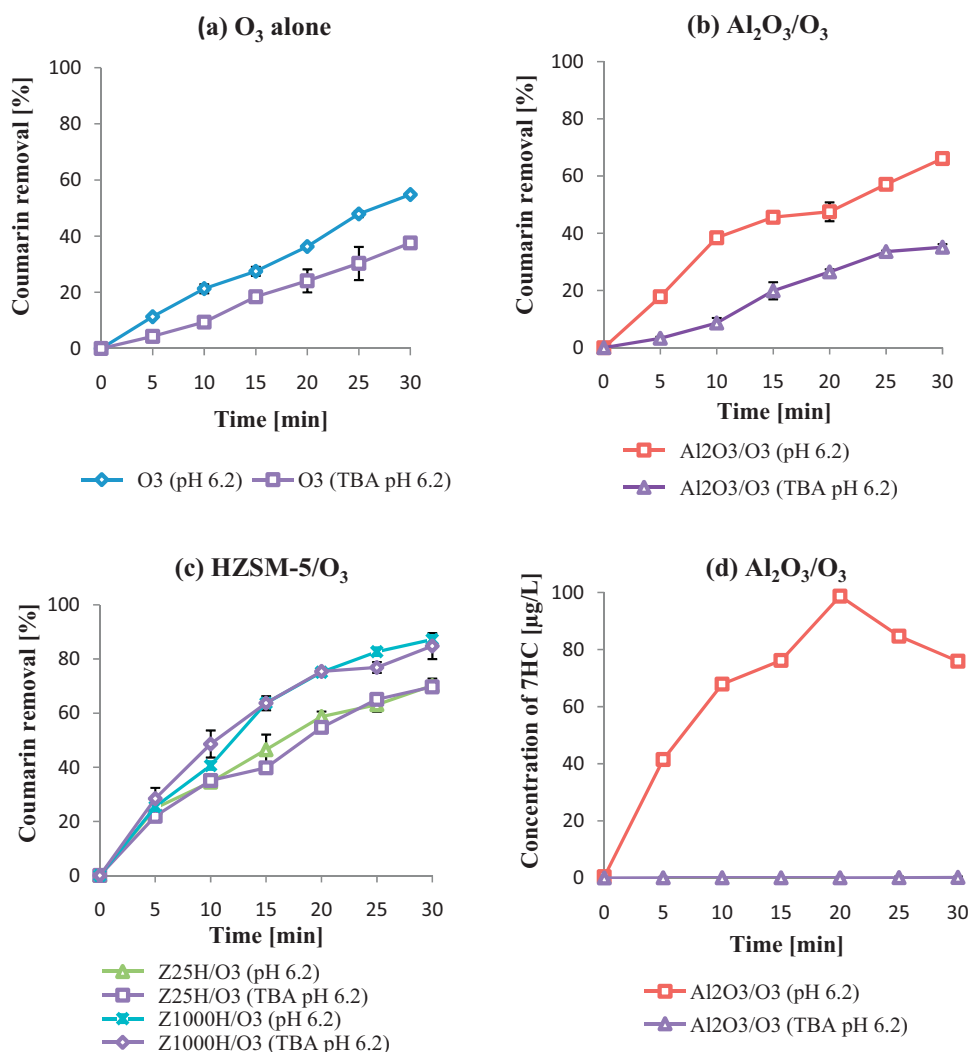
### 3.7. Effect of phosphates

Experiments with added phosphate ions (50 mg/L) were carried out on the basis that phosphate ions which are hard Lewis bases can displace hydroxide ions on the surface of alumina. These ions have high affinity towards alumina ions (Al) on the surface of alumina

[37] and their adsorption occurring through exchange of surface hydroxyl groups of alumina. This may verify the importance of hydroxyl groups present on the surface of alumina in ozone decomposition and to understand the possible influence of phosphates on ozonation in the presence of ZSM-5 zeolites.

Fig. 8 shows the effect of added phosphate ion on the rate of removal of coumarin at pH 6.2. In the presence of alumina, phosphate reduces the rate of coumarin removal (Fig. 8a). The effect of phosphate under zeolite catalysts is considerably less (Fig. 8b). Consistent with this is the extent to which phosphate ion is adsorbed by alumina compared to the zeolites which adsorb almost no phosphate (Fig. 8c). The data in Fig. 8d shows that 7HC production over alumina is reduced by phosphate, suggesting that phosphate poisons the surface sites responsible for the radical mechanisms – presumably hydroxyl groups. Overall adsorption of coumarin by both alumina and the zeolites is not affected significantly by phosphate, suggesting that only a small fraction on the adsorbed coumarin is linked to the critical sites for radical formation (Fig. 8e and f). This might suggest that hydroxyl groups on the surface of alumina might not be responsible for adsorption of COU but only ozone decomposition and hydroxyl radical formation





**Fig. 7.** Effect of TBA on the removal of coumarin by  $O_3$ ,  $Al_2O_3/O_3$  and HZSM-5/ $O_3$  ( $C_0(COU)$  = 20 mg/L; TBA = 50 mg/L;  $T$  = 25 °C; pH 6.2;  $O_3$  = 0.6 mg/min; catalyst = 2.0 g;  $V$  = 190 mL; SD  $\pm$  5%).

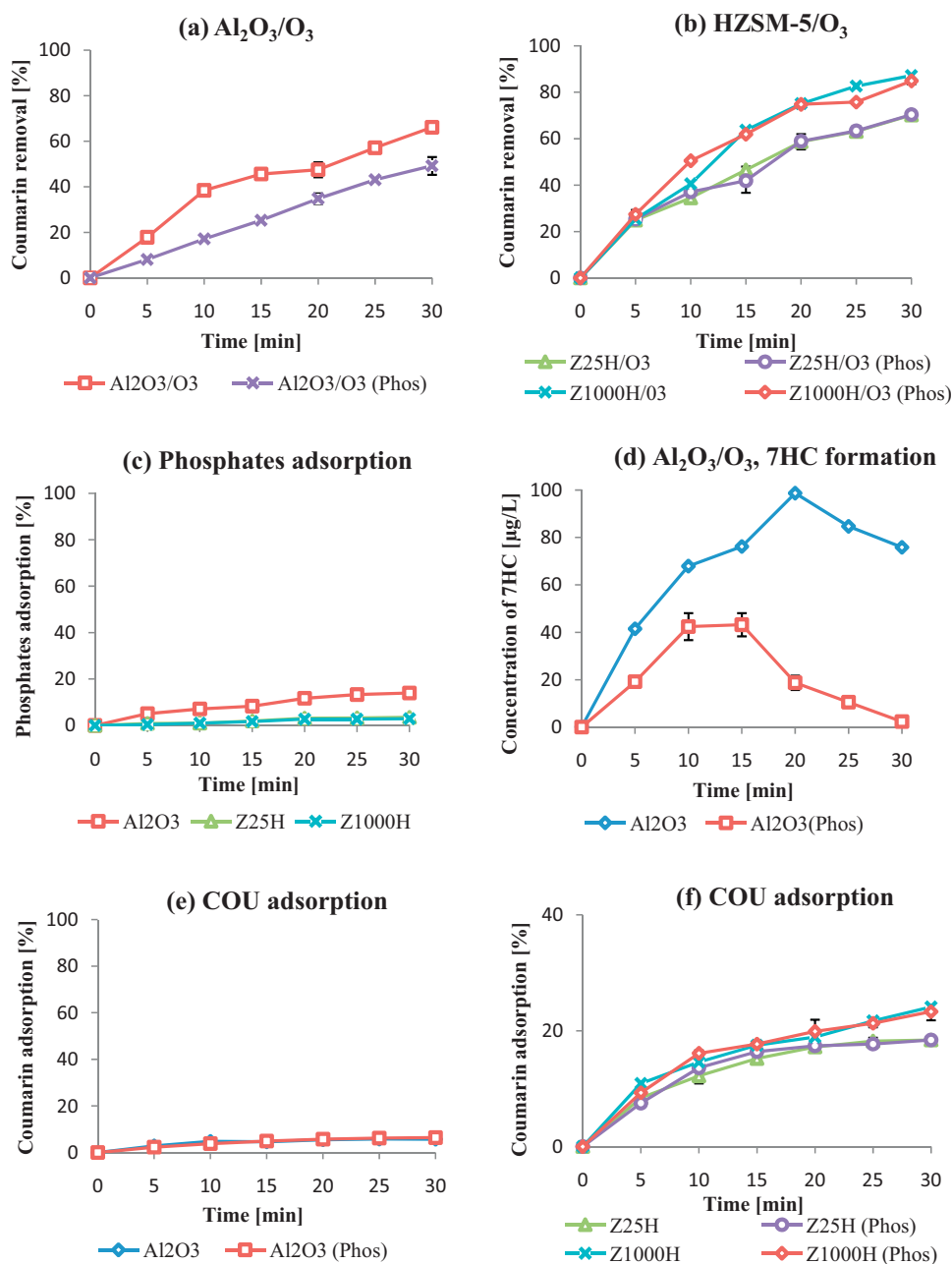
Similar results indicating the effect of phosphates on the catalytic activity of alumina have been reported by others. Beltran et al. [43] observed that the catalytic activity of alumina was greatly reduced in the presence of phosphates. Alvarez et al. [44] found that the presence of phosphates reduced the adsorption of pyruvic acid on the surface of alumina.

The effects of phosphate at other pHs appear in Fig. 9. The adsorption of phosphates on alumina increases with a decrease in the pH of solution and is highest at pH 3.0 (22% on 2.0 g of alumina in 30 min). Fig. 9c and d shows that the effect of phosphate on 7HC production over alumina is greatest at acidic pH. It seems reasonable to propose that at the lower pH, most of the hydroxyl radicals that take part on 7HC production are generated on the alumina surface, and so added phosphate reduces the rate of 7HC production significantly. As the pH is increased, two effects take hold. Firstly, the amount of phosphate adsorbed decreases and secondly because hydroxyl radicals formed from hydroxide ions in solution become increasingly important and adsorbed phosphate has no influence on these ions. It is important to note that the difference in efficiencies of COU removal in catalytic ozonation on alumina and ozonation alone were also the highest at pH 3 and this decreased with the increase in pH (Fig. 9b).

It is a well-known fact that different forms of phosphates exist at different pH ranges (these are  $H_3PO_4$ ,  $H_2PO_4^-$ ,  $HPO_4^{2-}$  and  $PO_4^{3-}$ ). Concentration of protonated forms of phosphates is the highest at acidic pH, hence the surface hydroxyl groups of alumina may be rapidly replaced at acidic pH as phosphates adsorption was considered to occur through exchange of surface hydroxyl groups of alumina [45]. The ligand exchange can also take place in the presence of water molecules and other easily displaced ligands coordinatively bonded to the sites [46]. The above results clearly indicate the importance of the effects phosphates (and other charged molecules with high affinity towards the surface of alumina) can have on the catalytic activity of materials used in catalytic ozonation of water micropollutants.

### 3.8. Effect of catalyst amount

In order to investigate the effect of catalyst amount on the efficiency of catalytic ozonation, HZSM-5 (Z1000H and Z25H) and alumina were studied. Ozonation experiments were performed in the presence of 2.0, 4.0 and 6.0 g of catalysts at pH 6.2. The results (Fig. 10) show an expected increase in COU removal with catalyst amount for both alumina and two



**Fig. 8.** Effect of phosphates on the removal of coumarin in  $\text{O}_3$ ,  $\text{Al}_2\text{O}_3/\text{O}_3$  and  $\text{ZSM-5}/\text{O}_3$  and adsorption of coumarin ( $C_0(\text{COU}) = 20 \text{ mg/L}$ ;  $\text{O}_3 = 0.6 \text{ mg/min}$ ;  $T = 25^\circ\text{C}$ ; pH 6.2; phosphates =  $50 \text{ mg/L}$ ; catalyst =  $2.0 \text{ g}$ ;  $V = 190 \text{ mL}$ ;  $\text{SD} \pm 3\%$ ).

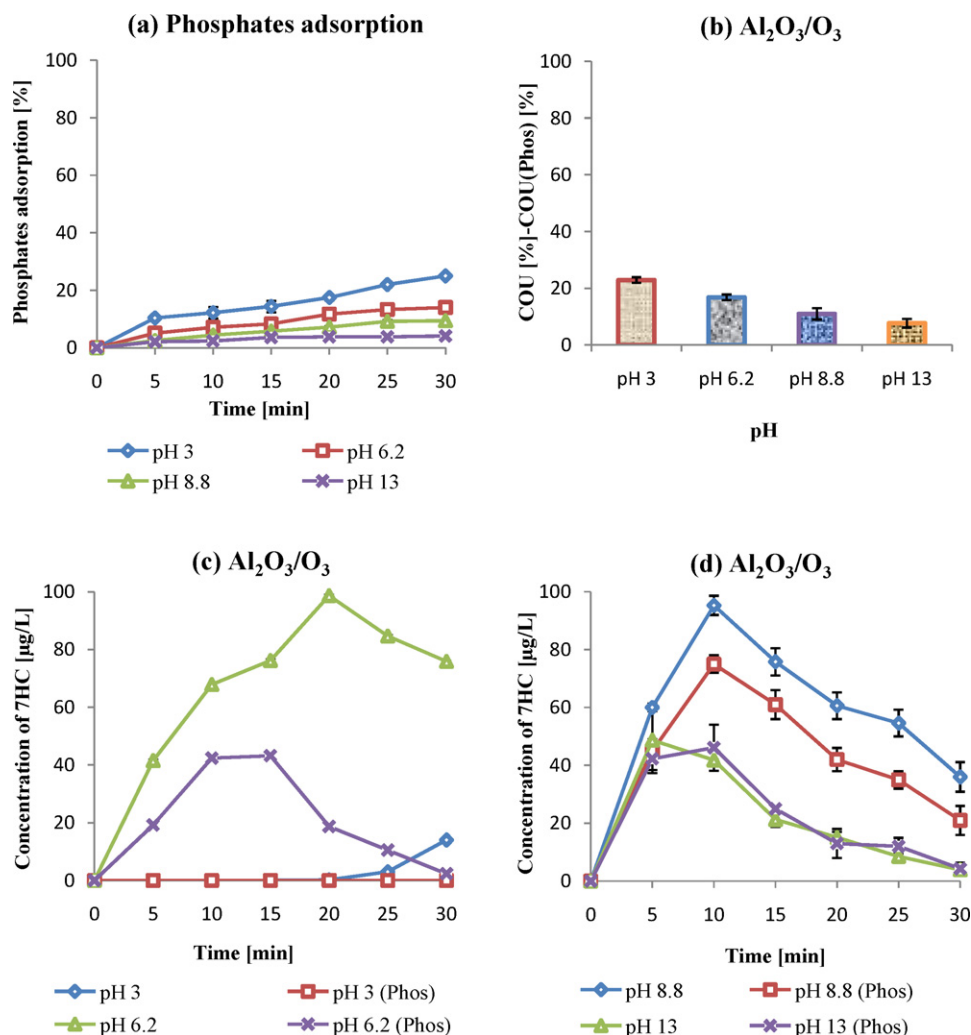
acidic zeolites. It has not been possible to reliably determine rates to establish the precise link between catalyst quantity and rate of removal but semi-quantitatively there seems to be close to a direct proportionality. This confirms that the degradation of coumarin occurs primarily on the catalyst surface at pH 6.2.

The yield of 7HC over alumina (Fig. 10d) also increases with catalyst amount, confirming that the decomposition route involving hydroxyl radicals also takes place only on the catalyst surface at this pH. With the highest catalyst amount there is some decrease in 7HC with time after the initial rise, and this suggests that in the presence of such a large amount of catalyst the 7HC itself can and does decompose.

### 3.9. Hydroxycoumarin ozonation

We have mentioned above that it appears that 7HC, the product of free radical decomposition of coumarin, might be decomposed itself over the catalysts used in this study. We have investigated this using solutions of 7HC exposed to ozonation in the presence of alumina and the Z25H and the Z1000H catalysts, and exposed to the same catalysts alone (to study simple adsorption of the 7HC on the catalyst surface). The results are presented in Fig. 11.

It is clear that none of these catalysts adsorb 7HC significantly (Fig. 11b). But all of them promote its removal, presumably degradation, by ozonation. Ozone alone is active in degrading 7HC but all four catalyst increase the rate of decomposition, with alumina



**Fig. 9.** Effect of pH and phosphates on the removal of coumarin in  $\text{Al}_2\text{O}_3/\text{O}_3$  and adsorption of coumarin ( $C_{0(\text{COU})} = 20 \text{ mg/L}$ ;  $\text{O}_3 = 0.6 \text{ mg/min}$ ;  $T = 25^\circ\text{C}$ ; pH 3.0, 6.2, 8.8 and 13.0; phosphates = 50 mg/L; catalyst = 2.0 g;  $V = 190 \text{ mL}$ ;  $\text{SD} \pm 3\%$ ).

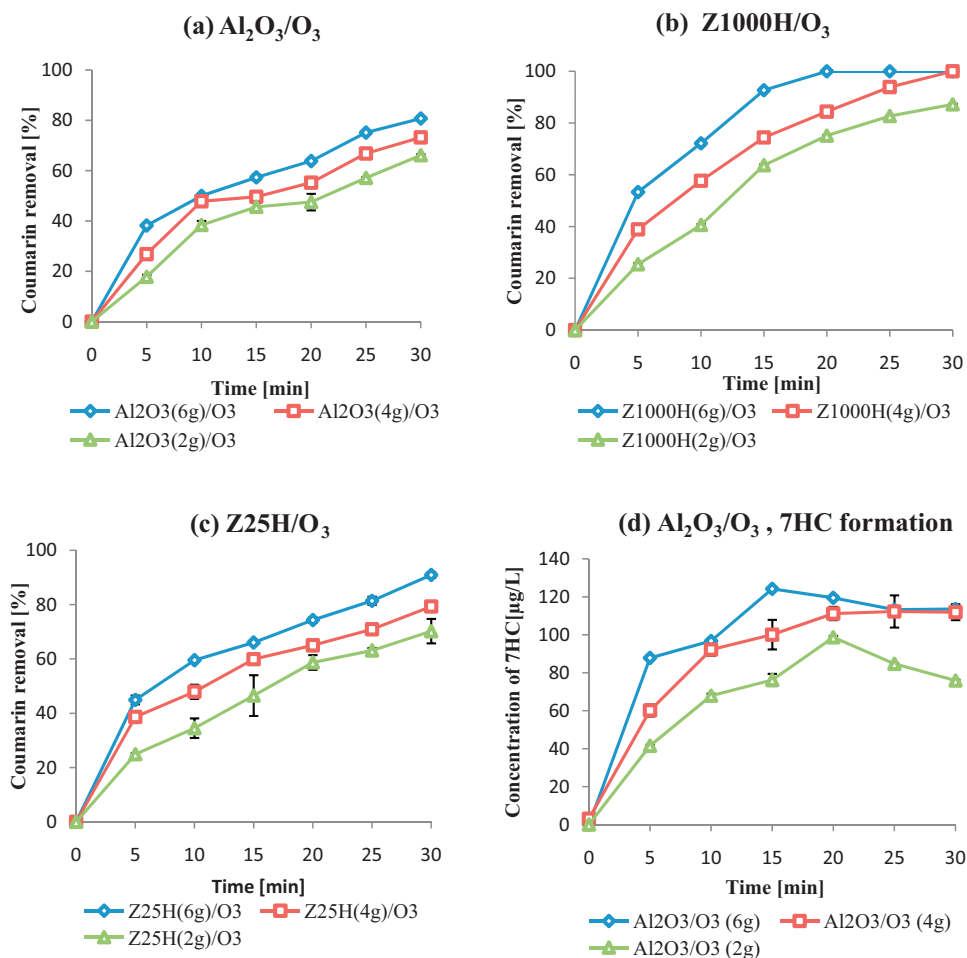
being very much more active than the two acid zeolites. This validates our earlier assumptions that decrease in 7HC concentrations after its formation from coumarin could be due to degradation by catalytic ozonation of 7HC, largely on the surface of the catalyst. The outcome of this study revealed that adsorption of coumarin and its transformation by-product, 7-hydroxycoumarin, is vital in catalytic processes and that catalytic ozonation of coumarin in the presence of alumina leads not only to the formation of its hydroxylated transformation by-products, but also its further degradation. It also explains why the observed formation of 7HC during ozonation of COU in the presence of alumina slows down and then decreases after a specific period of time (Fig. 5).

### 3.10. Suggested mechanism for ZSM-5 zeolites and alumina

Our results suggest that aqueous ozone can interact with surface hydroxyl groups of alumina, leading to the formation of hydroxyl radicals. The mechanism for this process has been proposed by others and involves intermediate formation of an  $\text{O}_2\text{H}^-$  anion, which then reacts with another ozone molecule to produce an  $\text{O}_3^-$  radical. It is then this ozonid radical that decomposes into an oxygen molecule and a hydroxyl radical. It is this hydroxyl radical that then oxidizes the organic compound. A similar mechanism was

suggested by Ernst et al. [25]. They also suggested that adsorption of pollutants on the surface of alumina is not essential for this reaction route; in other words the hydroxyl radical could react with the organic molecules in solution. Our results are not conclusive in this respect but it seems more likely to us that the eventual reaction with the organic molecule would take place on the catalyst surface than in the bulk solution. Our results do show that coumarin adsorbs on alumina and also that the adsorption sites are different to those that result in free radical formation (phosphate adsorption suppresses the latter but does not affect coumarin physisorption), so surface reaction would certainly be feasible.

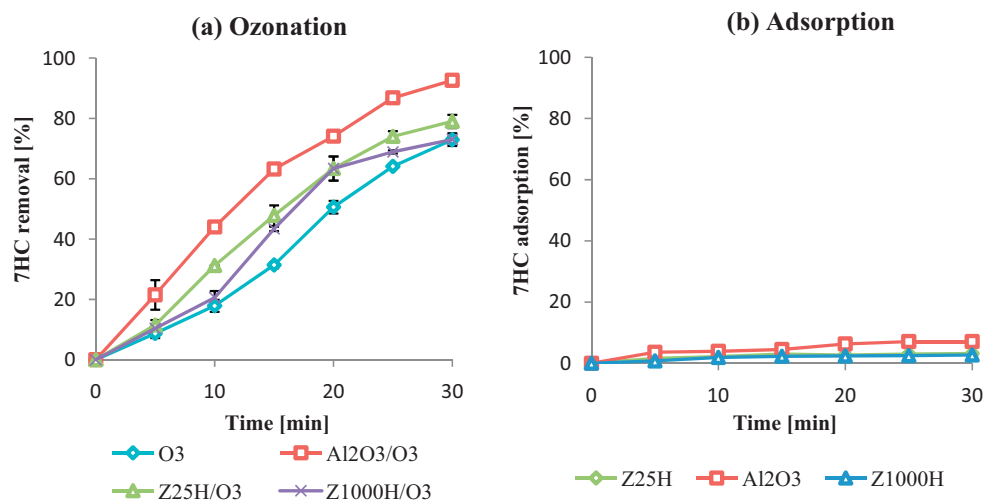
In the case of the zeolite catalysts we found the opposite to be the case, and that radicals are not involved in the catalytic ozonation process. The zeolites do catalyse the ozonation of coumarin however, but we propose that the zeolite acts simply as a reactive surface on which the reaction between  $\text{O}_3$  and the organic molecule can take place with reduced activation energy. All four zeolites adsorb coumarin effectively so the evidence for this suggestion is strong. At high pH in the presence of zeolites, the relative role of the catalyst becomes unimportant as a radical process starting from hydroxide ions in solution takes over.



**Fig. 10.** Effect of catalyst amount on the removal of coumarin by  $\text{Al}_2\text{O}_3/\text{O}_3$  and  $\text{HZSM-5}/\text{O}_3$  ( $C_{0(\text{COU})} = 20 \text{ mg/L}$ ;  $T = 25^\circ\text{C}$ ;  $\text{pH} 6.2$ ;  $\text{O}_3 = 0.6 \text{ mg/min}$ ; catalyst dose = 2.0 g, 4.0 g and 6.0 g;  $V = 190 \text{ mL}$ ;  $\text{SD} \pm 4\%$ ).

Within the family of ZSM-5 zeolites, the silica to alumina ratio has a significant but relatively small effect, in that the more hydrophobic materials with high silica contents tend to adsorb more coumarin (and presumably other relatively non-polar compounds) and so are more active in the removal of

coumarin by surface reaction. The fact that the hydrogen and sodium forms of the zeolite behave indistinguishably suggests that surface acid sites are not involved in the ozonation reactions, and the ozone reaction with the organic molecule is relatively simple.



**Fig. 11.** Removal of 7-hydroxycoumarin by  $\text{O}_3$ ,  $\text{Al}_2\text{O}_3/\text{O}_3$  and  $\text{ZSM-5}/\text{O}_3$  ( $C_{0(7\text{HC})} = 20 \text{ mg/L}$ ;  $T = 25^\circ\text{C}$ ;  $\text{pH} 6.2$ ;  $\text{O}_3 = 0.6 \text{ mg/min}$ ; catalyst = 2.0 g;  $V = 190 \text{ mL}$ ;  $\text{SD} \pm 2\%$ ).

## 4. Conclusions

The overall conclusions of this work are as follows.

- 1 Ozone degradation of coumarin in the presence of alumina occurs by a radical mechanism, almost certainly involving hydroxyl radicals, which are formed by reaction between ozone and surface hydroxyl groups (which are most reactive at pH close to the  $\text{pH}_{\text{PZC}}$ ).
- 2 ZSM-5 zeolites are also effective in the catalytic ozonation of coumarin but they do not act through a radical mechanism. Their activity arises through their ability to adsorb ozone and coumarin and so promote a surface reaction between the two molecules. Activity is independent of zeolite acidity, supporting this view. Activity shows some dependence on the hydrophobicity of the zeolite, with the more hydrophobic materials adsorbing more coumarin and hence showing higher activity towards its decomposition.

## Acknowledgements

The financial support from Higher Education Commission of Pakistan, the University of Engineering and Technology, Lahore (Pakistan) and the University of Huddersfield (UK) are gratefully acknowledged.

## References

- [1] S. Echigo, H. Yamada, S. Matsui, S. Kawanishi, K. Shishida, *Water Science and Technology* 34 (1996) 81–88.
- [2] A. Rathi, H.K. Rajor, R.K. Sharma, *Journal of Hazardous Materials* 102 (2003) 231–241.
- [3] E.J. Rosenfeldt, K.G. Linden, S. Canonica, U. von Gunten, *Water Research* 40 (2006) 3695–3704.
- [4] T.K. Lau, W. Chu, N. Graham, *Water Research* 41 (2007) 765–774.
- [5] B. Kasprzyk-Hordern, U. Raczyk-Stanislavski, J. Swietlik, J. Nawrocki, *Applied Catalysis B: Environmental* 62 (2006) 345–358.
- [6] B. Kasprzyk-Hordern, P. Andrzejewski, A. Dabrowska, K. Czaczky, J. Nawrocki, *Applied Catalysis B: Environmental* 51 (2004) 51–66.
- [7] Y. Yang, J. Ma, Q. Qin, X. Zhai, *Journal of Molecular Catalysis A: Chemical* 267 (2007) 41–48.
- [8] B. Kasprzyk-Hordern, M. Ziolek, J. Nawrocki, *Applied Catalysis B: Environmental* 46 (2003) 639–669.
- [9] J. Nawrocki, B. Kasprzyk-Hordern, *Applied Catalysis B: Environmental* 99 (2010) 27–42.
- [10] G. Jones, L. Indig, *New Journal of Chemistry* 20 (1996) 221–232.
- [11] D. Clark, J. Jimenez-Morais, G. Jones, E. Zanardi-Lamardo, C.A. Moore, R.G. Zika, *Marine Chemistry* 78 (2002) 121–135.
- [12] J.A. Leenheer, J.-P. Croua, *Environmental Science & Technology* 37 (2003) 18–26.
- [13] J. Oldenburg, E.-M. Quenzel, U. Harbrecht, A. Fregin, W. Kress, C.R. Müller, H.-J. Hertfelder, R. Schwaab, H.-H. Brackmann, P. Hanfland, *British Journal of Haematology* 98 (1997) 240–244.
- [14] C.H. Tsai, A. Stern, J.F. Chiou, C.L. Chern, T.Z. Liu, *Journal of Agricultural and Food Chemistry* 49 (2001) 2137–2141.
- [15] A.I. Okezie, P. Lester, *Methods in Enzymology* 2003 (1994) 57–66.
- [16] G.L. Newton, J.R. Milligan, *Radiation Physics and Chemistry* 75 (2006) 473–478.
- [17] T. Hirakawa, Y. Nosaka, *Langmuir* 18 (2002) 3247–3254.
- [18] K.I. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, *Electrochemistry Communications* 2 (2000) 207–210.
- [19] G. Louit, S. Foley, J. Cabillic, H. Coffigny, F. Taran, A. Valleix, J.P. Renault, S. Pin, *Radiation Physics and Chemistry* 72 (2005) 119–124.
- [20] H. Czili, A. Horváth, *Applied Catalysis B: Environmental* 81 (2008) 295–302.
- [21] J. Yu, L. Qi, M. Jaroniec, *the Journal of Physical Chemistry C* 114 (2010) 13118–13125.
- [22] C. Cooper, R. Burch, *Water Research* 33 (1999) 3695–3700.
- [23] F. Qi, B. Xu, Z. Chen, J. Ma, *Water Environment Research* 81 (2009) 592–597.
- [24] B. Kasprzyk, J. Nawrocki, *Ozone: Science and Engineering* 24 (2002) 63–68.
- [25] M. Ernst, F. Lurot, J.-C. Schrotter, *Applied Catalysis B: Environmental* 47 (2004) 15–25.
- [26] L. Chen, F. Qi, B. Xu, Z. Xu, J. Shen, K. Li, *Water Science and Technology: Water Supply* 6 (2006) 43–51.
- [27] F. Qi, B. Xu, Z. Chen, J. Ma, D. Sun, L. Zhang, *Separation and Purification Technology* 66 (2009) 405–410.
- [28] F. Qi, Z. Chen, B. Xu, J. Shen, J. Ma, C. Joll, A. Heitz, *Applied Catalysis B: Environmental* 84 (2008) 684–690.
- [29] J. Lin, A. Kawai, T. Nakajima, *Applied Catalysis B: Environmental* 39 (2002) 157–165.
- [30] H. Fujita, J. Izumi, M. Sagehashi, T. Fujii, A. Sakoda, *Water Research* 38 (2004) 159–165.
- [31] N.A.S. Amin, J. Akhtar, H.K. Rai, *Chemical Engineering Journal* 158 (2010) 520–527.
- [32] V.S.R. Rajasekhara Pullabhotla, S.B. Jonnalagadda, *Industrial & Engineering Chemistry Research* 48 (2009) 9097–9105.
- [33] H. Fujita, J. Izumi, M. Sagehashi, T. Fujii, A. Sakoda, *Water Research* 38 (2004) 166–172.
- [34] Standard Methods for the examination of water and waste water, (2005).
- [35] T. Preocanin, N. Kallay, *Croatia Chemical Acta* 79 (2006) 95–106.
- [36] J. Staehelin, J. Hoigne, *Environmental Science & Technology* 16 (1982) 676–681.
- [37] B. Kasprzyk-Hordern, *Advances in Colloid and Interface Science* 110 (2004) 19–48.
- [38] H. Valdés, V.J. Farfán, J.A. Manoli, C.A. Zaror, *Journal of Hazardous Materials* 165 (2009) 915–922.
- [39] A. Jentys, G. Warecka, M. Derewinski, J.A. Lercher, *Journal of Physical Chemistry* 93 (1989) 4837–4843.
- [40] D.H. Olson, W.O. Haag, W.S. Borghard, *Microporous and Mesoporous Materials* 35–36 (2000) 435–446.
- [41] G.V. Buxton, *Journal of Physical and Chemical Reference Data* 17 (1988) 513.
- [42] J. Hoigne, H. Bader, *Water Research* 17 (1983) 173–183.
- [43] F.J. Beltrán, F.J. Rivas, R. Montero-de-Espinosa, *Applied Catalysis B: Environmental* 47 (2004) 101–109.
- [44] P.M. Álvarez, F.J. Beltrán, J.P. Pocostales, F.J. Masa, *Applied Catalysis B: Environmental* 72 (2007) 322–330.
- [45] S. Tanada, M. Kabayama, N. Kawasaki, T. Sakiyama, T. Nakamura, M. Araki, T. Tamura, *Journal of Colloid and Interface Science* 257 (2003) 135–140.
- [46] J. Nawrocki, C. Dunlap, A. McCormick, P.W. Carr, *Journal of Chromatography A* 1028 (2004) 1–30.